

## Stable Water Isotope Inputs Across Mountain Landscapes

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### Abstract

Stable isotopes of water are important tracers in hydrologic research for understanding water partitioning between vegetation, groundwater, and runoff, but are rarely applied to large watersheds with persistent snowpack and complex topography. We combined an extensive isotope dataset with a coupled hydrologic and snow isotope fractionation model to assess mechanisms of isotopic inputs into the soil zone and implications on recharge dynamics within a large, snow-dominated watershed of the Upper Colorado River Basin. Results indicate seasonal isotopic variability and isotope lapse rates of net precipitation are the dominant control on isotopic inputs to the basin. Snowpack fractionation processes account for <5% annual isotope influx variability. Isotopic fractionation processes are most important in the shrub-dominated upper montane. Effects of isotopic fractionation are less important in the low-density conifer forests of the upper subalpine due to vegetative shading, low aridity, and a deep, persistent snowpack that buffers small sublimation losses. Melt fractionation can have sub-seasonal effects on snowmelt isotope ratios with initial snowmelt depleted but later snowmelt relatively enriched in heavy isotopes through the isotopic mass balance of the remaining snowpack, with the efficiency of isotopic exchange between ice and liquid water declining as snow ablation progresses. Hydrologic analysis indicates maximum recharge in the upper subalpine with wet years producing more isotopically depleted snowmelt (1-2‰ reduction in  $^{18}\text{O}$ ) through reduced aridity when energy-limited. The five-year volume-weighted  $^{18}\text{O}$  in this zone ( $18.2 \pm 0.4\text{‰}$ ) matches groundwater observations from multiple deep wells, providing evidence that the upper subalpine is a preferential recharge zone in mountain systems.

**Keywords:** stable isotopes of water, d-excess, snow dynamics, fractionation, mountain hydrology, recharge

### Key points

- A data-model framework explores hydrologic processes and snowpack fractionation on stable water isotopic inputs in complex topography.
- Snow fractionation accounts for <5% variability in isotopic loading. It is most important in the upper montane and minimal in the upper subalpine.
- Depleted snowmelt isotopic values in the upper subalpine match observed groundwater data suggesting this is a preferential recharge zone.

## 1. INTRODUCTION

Snow-dominated headwaters provide water resources to one-sixth the world’s population (Barnett, Adam and Lettenmaier, 2005) and support a wide range of ecologic and social-economic services (Immerzeel *et al.*, 2020). Although mountain systems are considered especially vulnerable to climate change (Hock *et al.*, 2019; Milly and Dunne, 2020), downgradient dependence on these resources is expected to increase in the near future (Viviroli *et al.*, 2020). There is growing awareness that groundwater is an important component of streamflow emerging from mountain systems (Miller *et al.*, 2016; Somers and McKenzie, 2020) and this water source has the potential to buffer climate extremes and enhance downstream resilience for water management (Taylor *et al.*, 2012). However, quantifying groundwater recharge and its linkage to snow processes is difficult in mountain systems, where steep terrain and difficult access typically limit the spatiotemporal resolution of data needed to quantify snow distribution and melt, evapotranspiration (ET) and subsurface heterogeneity. As a result, quantifying recharge in mountain systems remains uncertain (Meixner *et al.*, 2016).

Stable isotopes of water ( $^{18}\text{O}/^{16}\text{O}$ ,  $^2\text{H}/^1\text{H}$ ) have long been used as a natural tracer to assess water partitioning between ET, groundwater recharge and runoff (Vreča and Kern, 2020) and residence time distributions (McGuire and McDonnell, 2006) with work primarily at relatively small scales (<100 km<sup>2</sup>) (Vitvar, Aggarwal and McDonnell, 2005; Birkel and Soulsby, 2015) and in rain-dominated systems (e.g. Knapp *et al.*, 2019). Watersheds reliant on snow water inputs, however, alter the timing of water inputs through snow storage and may produce a different oxygen and hydrogen isotopic input signal as a function of post-depositional metamorphism in the snowpack. A comprehensive review on snow processes affecting isotopic characteristics in snowpack and associated snowmelt is provided by Beria *et al.* (2018). In short, oxygen and hydrogen isotopic composition of precipitation inputs depend on temperature, relative humidity, and origin of the air mass. This produces sub-seasonal storm variability and strong altitudinal effects; but in general, heavy isotopes in precipitation are at a maximum in summer and minimum in winter (Clark and Fritz, 1997). After deposition, the  $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$  ratios in the snowpack can vary due to diffusional transport of water from the soil, temperature-gradient induced vapor diffusion within the snow column, lateral flow through the snowpack and fractionation processes associated with sublimation, evaporation, and melt-freeze cycles (Stichler, Rauert and Martinec, 1981; Friedman *et al.*, 1991; Cooper, 1998; Sinclair and Marshall, 2008; Evans *et al.*, 2016; Beria *et al.*, 2018).

Sublimation effects on snowpack isotopic composition are most dominant during snowpack accumulation (Earman *et al.*, 2006) and preferentially enrich heavier isotopes on the snowpack surface (Stichler, Rauert and Martinec, 1981). Sublimation increases with low atmospheric pressure, low humidity, increased solar radiation and high wind speed (Earman *et al.*, 2006; Stigter *et al.*, 2018). Ice-to-vapor phase shifts are a kinetic process driven by molecular mass differentials between light and heavy water molecules (Clark and Fritz, 1997). This mass difference results in the snowpack being preferentially enriched in the heavier water molecules. Consequently, samples of partly evaporated snow will plot to the right of the meteoric water line in a  $^{18}\text{O}$ - $^2\text{H}$  diagram.

During snowpack ablation and periods of high solar radiation, melt fractionation becomes the dominant process of snowpack metamorphism (Earman *et al.*, 2006). Isotopic exchange between water and ice at  $0^\circ\text{C}$  produces a  $-3.0\text{‰}$  and  $-19.5\text{‰}$  for  $^{18}\text{O}$  and  $^2\text{H}$ , respectively, in water compared to ice (O’Neil, 1977). Subsequently, snowmelt is more depleted in  $^{18}\text{O}$  and  $^2\text{H}$  than the bulk snow from which it originates. From a mass balance perspective, the removal of depleted snowmelt produces a snowpack more enriched in  $^{18}\text{O}$  and  $^2\text{H}$  and as melt progresses, the snowpack, and corresponding snowmelt, become progressively enriched (Taylor *et al.*, 2001). The rate of isotopic exchange between water and ice is maximized when the snowpack is deep and the velocity of percolating water through the snowpack is low (Feng *et al.*, 2002). Kinetic processes of exchange during melt-freeze cycles in the snowpack are not large (Souchez *et al.*, 2000) and often disregarded.

Several studies have addressed the implications of snow processes on soil water isotopic influxes for source water mixing analysis (Cowie *et al.*, 2017; Carroll *et al.*, 2018; Zhang *et al.*, 2018) and a few studies have combined snow metamorphic processes with conceptual runoff models at catchment scales (Tetzlaff *et al.*, 2015; Ala-aho *et al.*, 2017). Only Stadnyk *et al.*, (2013) has created a large-scale ( $>1000\text{ km}^2$ ) and spatially distributed hydrologic and isotope model that included snowpack and snowmelt fractionation. This was done for seven dominant land classes to reduce equifinality in hydrologic model calibration but used a coarse 10-km spatial resolution. To our knowledge, no study has evaluated finely resolved spatial and temporal variability of isotopic compositions in snowpack across mountain landscapes. This is largely due to the difficulty of measuring sub-seasonal snowpack and snowmelt isotopic compositions across representative landscape units in which heterogenous topography and vegetation types may affect isotopic content. Ignoring the influences of snow storage and fractionation on isotopic boundary fluxes as a function of season, landscape position and climate could potentially introduce significant error to hydrologic analysis dependent on isotopic mass balance.

To assess isotopic inputs across steep topography, we use multiple years of stable water isotope data collected in precipitation, snowpack, and snowmelt to inform a coupled hydrologic and snowpack isotopic fractionation model of a Colorado River headwater basin and compare to local groundwater isotopic observations

(Williams et al., 2020). The approach tracks isotopic inputs into the soil zone at the daily timestep and 100 m spatial resolution in a basin with nearly 2 km in topographic relief. With this framework, we seek to answer the following questions: (1) What are the dominant mechanisms dictating water isotopic composition into the terrestrial system across mountain landscapes? (2) How does landscape position or climate condition affect isotopic influxes? (3) Can isotopic influx estimates help identify locations most important for groundwater recharge in mountain basins?

## 2. METHODS

### 2.1 Site Description

The Colorado River in the southwestern United States receives nearly 90% of its streamflow from snow-dominated headwater basins in Colorado, Wyoming and Utah (<https://www.usbr.gov/lc/region/g4000/contracts/watersource.html>) and is emblematic of arid and semi-arid river basins around the world that are reliant on snow-fed rivers for the bulk of their water (Viviroli, Weingartner and Messerli, 2003). Our study site, the East River, Colorado (ER, 750 km<sup>2</sup>, Figure 1) is representative of these critical headwater systems. An overview of the East River is provided by others (Carroll *et al.*, 2018; Hubbard *et al.*, 2018; Zhi *et al.*, 2020). The region is dominated by cold winters receiving approximately 80% of its water inputs via snowfall (October – May) and 20% from summer monsoon activity (July-September) (Carroll, Gochis and Williams, 2020). Elevations span 2500-4300 m. Conifer forests consist primarily of Engelmann Spruce-Subalpine Fir, with a smaller component of Blue Spruce, Douglas Fir, Lodgepole Pine, and Limber Pine. Deciduous Quaking Aspen forests and forb-dominated meadows occupy the lower elevations of the subalpine zone (2500 to 3200 m). Narrow-leaf Cottonwood and Willow species predominate along riparian corridors below 2600 m, while lower elevations (2400 to 2800 m) contain xeric shrublands, with Mountain Big Sagebrush, Black Sagebrush, Antelope Bitterbrush, Rocky Mountain Juniper, Gambel Oak, and native bunchgrasses interspersed with scattered Pinyon and Ponderosa Pine. Ecozones are broadly defined by elevation and dominant vegetation cover. Montane conditions (<3000 m) are dominated by shrubs, grasses and forbs; subalpine is predominantly conifer forest (3000-3700) while the alpine (>3700 m) is above treeline. The transition zone between the subalpine and alpine contains low density conifer forests, shrubs and barren ground is referred to as the upper subalpine.

### 2.2 Observations

#### 2.2.1 Hydrologic Data

Precipitation and air temperature observations were obtained from two snow-telemetry (SNOTEL) stations located in/near the ER, while daily observations of solar radiation and snow depth were collected from four stations operated by the Rocky Mountain Biological Laboratory (Figure 1, RMBL, <https://www.digitalrmbbl.org/collections/weather-stations/>). The spatial distribution of snow depth at the 3 m resolution was obtained from light detection

and ranging (LiDAR)-based Airborne Snow Observatory (ASO, Painter et al., 2016) flown 4 April 2016, 30 March 2018, 24 May 2018 and 7 April 2019. Snow depths were converted to snow water equivalent (SWE, 50 m) using ground observations and snow density modelling following Marks et al. (1999). Water years considered in this study (2015-2020) capture interannual variability observed in the SNOTEL period of record with 2016 representing average climate conditions, and 2018 and 2019 representing dry and wet climate conditions, respectively (Figure 2). Water year 2015 represents dry conditions but experienced large snowfall in May, stabilizing SWE late into the spring at higher elevations. Spatial observations from ASO near peak SWE in the basin illustrate differences in snow accumulation between a dry and wet water year, but in both cases the deepest snowpack resides at high elevation with emphasis on northern aspects in cirque valleys. Stream discharge was monitored by the Lawrence Berkeley National Laboratory Watershed Function Science Focus Area at 11 locations (Figure 1, SFA, Carroll and Williams, 2019; Carroll et al., 2021) and four locations managed by the United States Geological Survey (Figure 1, USGS, <https://maps.waterdata.usgs.gov/mapper/index.html>).

### 2.2.2 Stable Water Isotopes

We measured stable isotope ratios ( $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$ ) in precipitation, snowpack and snowmelt. We collected precipitation at site LMWL (Figure 1) from August 2014 to August 2016 and identified if precipitation was rain or snow. Three snowfall sampling sites were established October 2020 for weekly aggregated snow collection across an elevation gradient (Figure 1, IRN, LMWL, Estes) as part of the USGS Next Generation Water Observation System (NGWOS). Collectors were 1 m tall, 15 cm diameter PVC tubes with a capped bottom and 10 cm wire wind/bird baffle at the top. We dug snowpits in the years 2016-2020 (Figure 1) in flat areas and collected snow in 10 cm depth-resolved depth profiles for oxygen and hydrogen stable isotope analysis. Bulk samples represent a SWE-weighted isotopic composition across the snow column. We collected snowmelt at five locations (Figure 1) 2016-2017 using a modified version of Kormos (2005). Snowmelt was collected weekly beginning 1 April until full melt was achieved.

Water samples for stable isotope analysis were placed in 1.5 mL glass vials with Teflon<sup>TM</sup> coated septa lids. Hydrogen and oxygen isotope ratios of water were measured using an Off-Axis Integrated Cavity Output Spectrometer coupled to an auto-sampler interfaced with a heated injector block (Los Gatos Research, San Jose, USA). Hydrogen and oxygen isotope ratios are reported in conventional  $\delta$ -notation relative to Vienna Standard Mean Ocean Water scale. Groundwater data was collected by Williams et al. (2020) and processed in an identical manner. A commonly used index to assess deviation from the global meteoric water line (GMWL) is d-excess ( $\text{d-excess} = ^2\text{H} - 8 \cdot ^{18}\text{O}$ ) (Dansgaard, 1964). Observed samples with d-excess  $> 30\text{‰}$  or  $< -5\text{‰}$  were assumed anomalous or altered by post-collection evaporation and discarded. We used a total of 86 bulk snowpit samples and 56 snowmelt samples to constrain the isotope model.

### 2.3 Hydrologic Model

Our East River hydrologic model uses the semi-empirical, spatially distributed USGS code Precipitation-Modelling Runoff System (PRMS, Markstrom et al., 2015). Water and energy are tracked daily through the atmosphere, canopy and subsurface at a 100 m grid resolution for water years 2015 to 2020, with a one-year spin-up to stabilize subsurface water stores. Daily climate forcing assigns minimum and maximum temperature lapse rates from the two SNOTEL stations adjusted for aspect. Potential evapotranspiration (PET) is calculated using a modified version of the Jensen-Haise formulation dependent on temperature and solar radiation (Jensen, Rob and Franzoy, 1969). Solar radiation is based on a modified degree-day method developed in the Rocky Mountain region and applicable for sites with clear skies on days that lack precipitation (Leavesley *et al.*, 1983). The 2019 LiDAR-derived SWE, corrected for simulated losses from melt, canopy interception and sublimation, was used to spatially distribute snowfall. Rain was distributed using the Parameter-elevation Relationships on Independent Slopes Model (PRISM, 800 m), 30-year monthly averages for 1981-2010 (OSU, 2012). Precipitation phase (rain, snow) for a given location is controlled by a user-defined temperature threshold.

PRMS estimates snow accumulation and depletion for each model cell using a two-layer assumption accounting for radiant, convective and conductive exchanges as well as sublimation (Obled and Rosse, 1977). Snow storage is tracked as either solid or liquid with the amount of free liquid a function of the energy balance and physical properties of the snowpack. A precipitation event occurring at a temperature other than freezing will affect the energy storage of the snowpack. The reference energy state, or an all-ice, isothermal condition is 0°C. When the snowpack lacks enough heat to be isothermal its temperature drops below 0°C and this is tracked as an energy deficit, or the amount of energy per unit area to bring the snowpack back to isothermal. When the snowpack energy is above the reference state, some ice will melt and produce some amount of free water based on the latent heat of fusion of water. If the volume of free water exceeds the pore space of snowpack, then the snowmelt and latent energy from snowpack storage exits the snowpack.

Precipitation contributes water to the snowpack and adds/subtracts energy content based on its phase and temperature. Change in snow covered area uses a depletion curve approach to account for sub-grid heterogeneity in melt (Anderson, 1973), while albedo is a function of incoming solar radiation and decay-curves defining the accumulation and melt periods of seasonal snowpack ripening. Shortwave radiation at the snowpack surface is limited by the winter vegetation transmission coefficient and reduced by the estimated albedo. Incoming longwave radiation is an empirical relationship based on winter vegetation cover density and air temperature, while outgoing longwave radiation from the snowpack is assumed a perfect blackbody based on the surface temperature of the snowpack. Convection and latent heat from condensation are assumed a function of air temperature and only applied when there is precipitation, and

the air temperature is  $>0^{\circ}\text{C}$  as surrogates for sufficient vapor pressure to allow. Trees and shrubs are assumed to diminish wind and the energy applied to the snowpack in these areas is diminished by half. Sublimation is calculated with a user-defined fraction of PET adjusted for head deficit in the snowpack and snow-covered area.

Vegetation cover type at the 1 m resolution (Breckheimer, 2021) was overlain with the USGS Landfire (2015) 30 m resolution meadow and then resampled to the 100 m grid (refer to Figure 5a). PRMS parameters for summer and winter cover density, canopy interception characteristics for snow and rain, and transmission coefficients for short wave solar radiation relied on Landfire (2015). Net precipitation is the amount of rain/snow that moves through the canopy and reaches the ground. It is a function of available canopy storage related to precipitation phase, canopy density and leaf/needle water holding capacity. Canopy storage losses can only occur through evaporation as a function of PET. If storage is at a maximum and losses to evaporation do not occur, then net precipitation equals precipitation.

Maximum soil water storage is a field capacity above which water is partitioned to either lateral interflow through the soil zone or vertical flow via gravity drainage to deeper subsurface storage. The spatial distribution of maximum soil storage was calculated as the product of rooting depth (Landfire, 2015) and available water content as a function of soil type (NRCS, 1991). Groundwater inflows to a given cell account for excess soil water, gravity drainage, and up-slope contributions while outflows are a simple linear function of groundwater storage. Parameters related to solar radiation, PET, soil storage and groundwater transmissivity were adjusted to best match observed solar radiation and stream discharge. Model validation uses 2016 and 2018 ASO-derived SWE, snow pit SWE, snow depth at the RMBL weather stations and ET at the flux tower (Ryken, Gochis and Maxwell, 2020). Daily water influxes into the soil are defined as snowmelt plus rain when  $\text{SWE} = 0$ . Rain falling on existing snowpack is accounted for in the water and energy calculations of the snowpack with the potential to generate snowmelt.

## 2.4 Water Isotope Mass Balance Model

The isotope mass balance model follows Ala-aho et al. (2017) to track  $^{18}\text{O}$  entering the soil system as snowmelt or rain, and was expanded to include  $^2\text{H}$  and d-excess as well as kinetic fractionation and melt fractionation efficiency. Precipitation isotope inputs ( $P^i$ , ‰) are spatially distributed using,

$$P_{x,1,t}^i = P_{x,3,t}^i + 8P_{x,2,t}^i \quad (1a)$$

$$P_{x,2,t}^i = P_{p,2,t}^i + \lambda_o (E_x - E_p) / 100 \quad (1b)$$

$$P_{x,3,t}^i = P_{p,3,t}^i + \lambda_d (E_x - E_p) / 100 \quad (1c)$$

Where,  $E$  is elevation (m);  $\lambda_o$  and  $\lambda_d$  (‰ per 100 m) are precipitation lapse rates for  $^{18}\text{O}$  and d-excess, respectively;  $x$  designates input location,  $p$  is the location

of LMWL;  $t$  is time (day) and subscripts 1 =  $^2\text{H}$ , 2 =  $^{18}\text{O}$  and 3 = d-excess.

$^{18}\text{O}$  and  $^2\text{H}$  values of sublimated vapor from the snow surface ( $S^i$ , ‰) are calculated as,

$$S_{x,1,t}^i = (S_{x,1,t-1}^i - 8\varepsilon)(1 + \kappa) \quad (2a)$$

$$S_{x,2,t}^i = S_{x,2,t-1}^i - \varepsilon, \quad (2b)$$

$$S_{x,3,t}^i = S_{x,1,t}^i + 8S_{x,2,t}^i \quad (2c)$$

Where (‰) is the isotopic exchange parameter for  $^{18}\text{O}$  between ice and vapor (Ala-aho *et al.*, 2017) and kinetic exchange during evaporation ( , dimensionless) estimates  $^2\text{H}$  based on deviation from the GMWL.

Isotopic delta values of snowmelt ( $M^i$ , ‰) are calculated similar to Ala-aho *et al.*, (2017) but includes melt fractionation efficiency ( , dimensionless).

$$M_{x,1,t}^i = M_{x,1,t-1}^i - 8\mu\phi_{x,t} \quad (3a)$$

$$M_{x,2,t}^i = M_{x,2,t-1}^i - \mu\phi_{x,t} \quad (3b)$$

$$M_{x,3,t}^i = M_{x,1,t}^i + 8M_{x,2,t}^i \quad (3c)$$

With (‰) representing maximum isotopic exchange of  $^{18}\text{O}$  between ice and liquid water. The relative efficiency of exchange ranges from 0 to 1 based on the normalized metric,

$$\phi_{x,t} = \frac{\beta SWE_{x,t}}{M_{x,t}} \text{ if } \phi_{x,t} > 1, \quad \phi_{x,t} = 1 \quad (4)$$

where  $SWE$  (mm) and  $M$  (mm/day) are snow water equivalent and daily snowmelt, respectively, for a given model cell on a given day, and the coefficients  $\beta$  and  $\mu$  are constant values representing simulated average SWE and average melt rates in the ER.

Lastly, the bulk snowpack isotopic values ( $SN^i$ , ‰) are,

$$SN_{x,j,t}^i = \frac{SN_{x,j,t-1}^i SWE_{x,t-1} + P_{x,j,t}^i P_{x,t}^n - S_{x,j,t}^i S_{x,t} - M_{x,j,t}^i M_{x,t}}{SWE_{x,t-1} + P_{x,t}^n - S_{x,t} - M_{x,t}} \quad (5a)$$

$$SN_{x,3,t}^i = SN_{x,1,t}^i - 8SN_{x,2,t}^i \quad (5b)$$

Where  $j = 1$  or  $2$ ;  $P^n$ ,  $S$  are daily net precipitation and sublimation (mm per day), respectively.

Water stores and fluxes needed for the isotopic model ( $SWE$ ,  $P^n$ ,  $S$  and  $M$ ) use hydrologic model output for each timestep and model grid location with  $\delta$  calculated from these hydrologic terms. Lapse rates ( $\delta_o$ ,  $\delta_d$ ) are based on observed data. Isotope model calibration was reduced to the three fractionation parameters ( $\kappa$ ,  $\varepsilon$ ,  $\mu$ ). These were estimated using a Monte Carlo approach with uniform input distributions and 1000 realizations.  $\kappa$  was assumed to fall between 0 and 3.5‰ and  $\varepsilon$  from 0‰ to 15‰ (Gat and Gonfiantini, 1981). Kinetic fractionation ( $\mu$ ) was allowed to search between -1 to 1.



Modelled results are compared to observed data at the location and date collected. The sampling location IRN and OP (Figure 1) fall slightly outside the model domain. They were repositioned into the domain by matching elevation, aspect, and vegetation type of the most proximal active cell. Model results are assessed using a relative root mean squared error (rRMSE) for each type of isotope ( $^2\text{H}$ ,  $^{18}\text{O}$ , d-excess) and type of observation (snowpack, snowmelt). The final parameter values are based on the average value obtained for the ten realizations with the lowest composite rRMSE. Effects of each fractionation parameter were isolated by running the model with calibrated parameters independently set to zero and comparing to the calibrated simulation.

### 3. RESULTS

#### 3.1.1 Observed Isotopic Data

Precipitation data collected at site LMWL exhibited direct linear relationships with mean daily temperature at the proximal SNOTEL (Figure 3). Slopes for the  $^{18}\text{O}$  and temperature relationship were steeper for rain than snow while the d-excess versus temperature showed a slightly positive slope for snow and sharply decreasing slope for rain with increasing temperature. These linear temperature functions defined precipitation inputs at site LMWL ( $P_{p,t}^i$ , equation 1) and resulted in seasonal oscillations of  $^{18}\text{O}$  ( $^2\text{H}$ ) from a maximum in July of 0‰ (0‰) to a minimum in December of -28‰ (-220‰). Linear lapse rates for  $^{18}\text{O}$  and d-excess were calculated from average weekly aggregated snowfall at three locations and equalled -0.16‰ and 0.96‰ per 100 m, respectively. Resulting seasonal variability in precipitation for years 2015-2020 at LMWL were estimated 207.8‰, 27.5‰ and 18.4‰ for  $^2\text{H}$ ,  $^{18}\text{O}$  and d-excess, respectively; while elevation lapse rates introduced variations in precipitation across the ER equal to 39.7‰, 2.8‰ and 17.3‰.

Analysis of snowpit depth-resolved and bulk isotopic observations collected over six years are provided in the Supporting Information (SI, Figure S1-S7). The temporal evolution of snowpack isotopic signatures in 2020 indicated the lower elevation snowpit began more depleted in  $^{18}\text{O}$  than the higher elevation snowpit but over time enriched 3x more quickly (Figure 4a). With respect to d-excess, the higher elevation site was approximately 15‰, and showed little variation over the snow accumulation and ablation period. In contrast, the lower elevation snowpit averaged -0.03‰ per day in d-excess with most of this reduction occurring late in the spring (Figure 4b). Initial snowmelt had lower  $^{18}\text{O}$  values compared to the snowpack near peak SWE. By late season, snowmelt was relatively enriched. The rate of snowmelt  $^{18}\text{O}$  variation ranged from 0.04 to 0.12‰ per day with snowmelt increasing by 3.4 to 5.4‰ over the duration of the melt period (Figure 4c). Enrichment in  $^{18}\text{O}$  was largest at lower elevations. Snowmelt d-excess decreased over time (-0.07 to -0.14 ‰ per day) with rates of decline highest at the lowest elevation (Figure 4d).

#### 3.1 Hydrologic Model

Near peak SWE, simulated snow accumulation mimicked observations with the deepest snowpack in the upper subalpine and along northern aspects, where both forest and topographic shading allow the snowpack to persist (Figure S8-S11). At lower elevations, mountain ridges, and southern aspects SWE was reduced or eliminated by early spring as a function of wind scour, sublimation, and early season snowmelt. Simulated SWE was within 100 mm of ground-based measurements, with bias in under prediction predominantly at lower elevations (Figure S12). Seasonal water inputs were largest in the spring and occurred predominantly in the upper subalpine (Figure S19). Sublimation was a relatively small proportion of the annual basin-scale water balance ( $2.4 \pm 0.3\%$ ), representing  $5.1 \pm 0.7\%$  of the total annual ET (Figure 5b). It was largest along southern aspects and at high elevations that were not shaded by forest vegetation. Canopy interception losses were also tracked and accounted for a substantially large proportion of annual ET ( $27 \pm 3\%$ ), or  $13 \pm 3\%$  of the basin’s water budget. These evaporative losses were not directly simulated in isotopic exchange with the underlying snowpack, but the timing and amount of this loss was tracked through the mass balance of isotopic water inputs via net precipitation (Figure S21).

### 3.2 Water Isotope Model

Monte Carlo composite rRMSE for all realizations are provided in the SI (Figure S17), with calibrated values given in Table 1. Model output was only moderately sensitive to snowmelt and evaporative fractionation, with the best realizations clustered at the low end of input distributions. Spatial distribution of volume-weighted  $^{18}\text{O}$  isotopic water influxes (snowmelt, rain) into the terrestrial system ranged from  $-10.6\text{‰}$  to  $-19.5\text{‰}$  (Figure 5c). The most enriched values occur in the montane and the most depleted values occur in the subalpine (Figure S19). Aggregated annually, isotopic inputs to the terrestrial system differ only slightly from net precipitation based on snow metamorphic processes (Figure 5d). Changes in annual input signatures related to snowpack fractionation were explored as a function of elevation, sublimation, annual snow fraction, aridity (ratio of potential ET to precipitation, or PET/P), cover type and aspect (Figure S22). Fractionation enriched the heavy oxygen isotope over net precipitation on the order of 0.2 to 0.4‰ (median) with spatial trends across the ER not well defined. However, on average, snowmelt enrichment was largest in the montane ( $<3000$  m) containing modest snow accumulation, water-limited conditions ( $\text{PET}/\text{P} > 1$ ), and along southern aspects. The least amount of snow fractionation occurred in the upper subalpine where low-density conifer forests, deep snowpack, energy-limited conditions ( $\text{PET}/\text{P} < 1$ ), and northern aspects occur.

We examined the temporal evolution of isotopic influxes at three locations over an average water year (refer to Figure 1 for locations). Location A is in the alpine (3878 m) with a southern exposure. Snowpack remained low but persisted into mid-spring (Figure 6a) with low snowmelt rates (Figure 6b) to produce moderate melt fractionation efficiencies over the snow ablation period ( $\tau = 0.30$ , Figure 6c). Location B is in the upper subalpine (3566 m) with a north-

ern exposure and a deep and persistent snowpack lasting into late spring with averaging 0.45 during ablation. Location C is in the montane (2705 m) with low snow accumulation, full melt in March and an average  $\delta = 0.36$  following peak SWE. Precipitation inputs indicate daily to seasonal swings in  $^{18}\text{O}$  as a function of air temperature, precipitation phase and elevation (Figure 6d) with  $^{18}\text{O}$  influxes to the soil zone mimicking these trends. The exception is with snow storage averaging precipitation inputs and delaying their release (Figure 6e). Focusing on snowmelt from peak SWE to SWE = 0,  $^{18}\text{O}$  influxes increased 4.9, 1.1 and 6.7‰  $^{18}\text{O}$  for sites A, B and C, respectively (Figure 6f). Slopes of enrichment span 0.02 to 0.13‰ per day. A sharp increase in  $^{18}\text{O}$  at location C is the result of a relatively large, warm snowstorm contributing enriched precipitation to a shallow, more depleted snowpack just prior to full snowpack loss. Rates of enrichment at these three locations showed no correlation to elevation or sublimation but were indirectly related to average  $\delta$  during ablation ( $r^2=0.98$ ,  $p=0.067$ ). Isolating the effects of melt fractionation (Figure 6g) resulted in an initially depleted snowmelt isotope ratios (-0.16‰  $^{18}\text{O}$ ) when maximum efficiency in liquid-ice exchange was achieved. Over time, melt fractionation produced a more positive ( $^{18}\text{O}$  enriched) signal compared to the scenario if no melt fractionation was simulated, with the amount of enriched snowmelt increasing in deeper, more persistent snowpack. Evaporative fractionation enriched  $^{18}\text{O}$  in snowmelt up to +0.2‰ at the montane site and at the south facing alpine site (Figure 6h) and decrease d-excess by -1.5‰ (Figure 6i). The effects of evaporative and kinetic fractionation were much lower for the north facing upper subalpine site.

Differences ( $\delta$ ) in isotopic boundary influxes between a wet (2019) and dry (2018) water year were explored by reducing to a single dimension of elevation (Figure 7a). Isotopic precipitation differences were removed to isolate the effects of land surface hydrological processes on isotopic inputs.  $^{18}\text{O}$  influxes to the soil of a wet year approached -2‰ at the highest elevations and +0.5‰ at the lowest elevations in comparison to a dry year. d-excess were low across all elevations except at the highest elevation in the basin where d-excess decreased by 0.6‰. Wet years had a larger amount of snow across all elevations, with the largest relative increase in the montane (Figure 7b), with PET decreasing with decreasing elevation (Figure 7c). The shift between energy- and water-limited conditions (PET/P=1) occurred at higher elevations for dry water years compared to wet water years (Figure 7d). Sublimation was lower in wet years compared to dry years where conditions were energy-limited, but at lower elevations wet years supported more sublimation due to increased snow availability (Figure 7e). Regression analysis on hydrologic characteristics most important to change in isotopic influx used correlation analysis and the Akaike Information Criterion (AIC) to assess if added parameters brought additional information given co-dependence between input parameters. Changes in SWE, PET, aridity and sublimation between water years (Figure 7f-m) describe most of the change ( $r^2=0.99$   $^{18}\text{O}$ ;  $r^2=0.83$  d-excess). Statistical significance was high for all parameters defining  $^{18}\text{O}$ , with the exception for changes in sub-

limation. Statistical significance were much lower for individual parameters defining d-excess.

Figure 8 compares the mean and standard deviation of recharge and volume-weighted isotopic inputs for water years 2016-2020 across elevation. The upper subalpine (3600-4000 m) was identified as the preferential recharge zone where recharge is at a maximum across a range of climate conditions just above treeline (Figure 8a). Within the preferential recharge zone, annual  $^{18}\text{O}$  influxes were  $18.2 \pm 0.4\text{‰}$  and aligned with observed groundwater data ( $18.2 \pm 0.4\text{‰}$ ) collected at three deep wells (80-100 m) and one perennial spring (Figure S23). Results indicate a more depleted signature in the subalpine that was approximately 2‰ lower than the montane and 1‰ lower than the alpine (Figure 8b). Water year 2015 was simulated  $+3.5\text{‰}$   $^{18}\text{O}$  compared to the 2016-2020 average largely due to its outsized reliance on late spring snowfall and movement toward more seasonally enriched precipitation input. This year was assumed anomalous, but if included then the influx of  $^{18}\text{O}$  into the preferential recharge zone becomes  $-17.8 \pm 1.1\text{‰}$  and still captures the range in groundwater observations. Simulated volume-weighted d-excess infiltrating the soil zone is simulated as strongly controlled by elevation (Figure 8c). Estimated d-excess in the preferential recharge zone is simulated at  $20.5 \pm 0.4\text{‰}$  and did not agree with observations in groundwater ( $10.7 \pm 1.8\text{‰}$ ).

#### 4. DISCUSSION

Isotopic fractionation processes in snow are fairly well defined (Beria *et al.*, 2018) but little work has addressed these processes at watershed-scales in mountain environments. Challenges are largely due to obtaining hydrologic and isotopic observations at the scales important to snow accumulation and ablation (Bales *et al.*, 2006; Clark *et al.*, 2011). Temporal scales are defined by meteorological inputs (hourly-daily) needed to quantify the energy balance of the snowpack, while the spatial resolution needed to capture non-uniform hydrologic processes in mountain systems is on the order of 100 to 250 m (Baba *et al.*, 2019; Foster, Williams and Maxwell, 2020). An added complication arises given most of the snow resides near treeline (Mott, Vionnet and Grünwald, 2018). Regular and safe access for field work in these environments is often not possible, field equipment installations struggle in the harsh climate (Varadharajan *et al.*, 2019) and use of satellite remote sensing techniques to retrieve snow mass in mountain systems remains problematic (Lettenmaier *et al.*, 2015).

Because of data collection challenges, mass-balance isotope mixing models in snow-dominated terrain tend to aggregate limited snow data to define simple oxygen and hydrogen stable isotope relationships between bulk snowpack to snowmelt runoff (Bearup *et al.*, 2014; Carroll *et al.*, 2018; Fang *et al.*, 2019). Time-variable isotopic inputs have largely been confined to laboratory experiments (Feng *et al.*, 2002; Taylor *et al.*, 2002) or to field studies focused on snowpit (Stichler, Rauert and Martinec, 1981; Friedman *et al.*, 1991; Taylor *et al.*, 2001) or hillslope (Evans *et al.*, 2016) scales. More recently, Ala-aho *et al.* (2017) incorporated changes in snow isotopic values with a snow process

model to estimate a spatially distributed snowmelt isotope signal. Their work represents a significant advancement in quantifying water mass influx using stable isotopes but was still limited to small ( $<4 \text{ km}^2$ ) and relatively low relief catchments ( $<440 \text{ m}$ ). No study has addressed the fine scales important to snow dynamics in high relief terrain across spatial scales important to water management ( $>100 \text{ km}^2$ ).

In an attempt to address scaling, we expanded the Ala-aho et al. (2017) parsimonious approach to explore the mechanisms driving stable water isotope inputs to a mountain watershed and the relative importance of snow fractionation processes on this loading signal. Finely resolved analysis (100 m, daily) allowed us to track meteorological inputs and snow dynamics across the basin accounting for steep topography and diverse vegetation structure. Hydrologic modelling recreated the spatial distribution of snow accumulation and persistence through use of LiDAR mapping and relied on climate and streamflow observation networks in its parameterization and evaluation. Extensive snow isotope data spanned elevations from 2700 to 3600 m, were collected over a 5-year period representative of climate across the historical record and were used to train the isotopic fractionation model. It is a bold approach, with several limitations (discussed below), but provides a first attempt in quantifying the relative importance of snow fractionation as a function of hydrology, landscape position and climate variability.

#### 4.1. Isotopic Variability across Mountain Landscapes

Seasonal variability and elevational lapse rates in precipitation’s isotopic composition were found to be the dominant mechanisms defining the stable water isotopic influx into the terrestrial system, with isotopic fractionation processes within the snowpack representing  $<5\%$  of this variability. Similar to Otte et al. (2017), the oxygen and hydrogen isotopic composition of precipitation was defined as a function of ambient air temperature and the phase of precipitation. These are surrogates for cloud condensation temperature (Dansgaard, 1964) and the Rayleigh effect along the air mass trajectory in which more water condenses in cold air to become more depleted in heavy isotopes, compared to rain forming in warmer conditions (Clark and Fritz, 1997; Beria *et al.*, 2018). Rainfall produced more enrichment in  $^{18}\text{O}$  for a given increase in temperature than for snow. Simultaneously, rain exhibited a rapid decrease in d-excess with increased air temperature. Both trends are indicative of evaporation of rain in transit from cloud to ground (Clark and Fritz, 1997) that are more pronounced under lower humidity, summer conditions within the ER. While statistically significant, there was a large amount of scatter in the linear regressions describing precipitation isotopic inputs. Error was due to the stochastic nature of weather, but also reflects a sampling strategy that did not aggregate across storm totals. As an example, on 9 September 2014, a single rainstorm was sampled at 1 to 3-hour intervals. Observed intra-storm variability equalled  $3.3\text{‰}$  ( $^{18}\text{O}$ ),  $28.4\text{‰}$  ( $^2\text{H}$ ) and  $12.0\text{‰}$  (d-excess) and are similar to those presented by others (Han *et al.*, 2020). However, it is argued that average behaviour is captured by the

large number of samples collected over multiple years ( $n=130$ ). Increased depletion in heavy isotopes with altitude has long been recognized as a consequence of the Rayleigh distillation effect (Dansgaard, 1964). Lapse rates for the ER Watershed used a limited data set, but trends for  $^{18}\text{O}$  ( $-0.16\text{‰}$  per 100 m) fall slightly below other studies in North America ( $-0.17$  to  $0.22\text{‰}$ , Friedman et al., 1992; Tappa et al., 2016) and the global average ( $-0.28\text{‰}$ , Poage and Chamberlain, 2001). In terms of d-excess, empirical fractionation experiments indicate low condensation temperatures at high elevations can increase values  $0.3\text{‰}$  per  $-1^\circ\text{C}$  (Majoube, 1971), which adjusted for observed temperature lapse rates in the ER, equates to a relatively low d-excess lapse rate ( $0.19\text{‰}$  per 100-m) in comparison to those observed ( $0.96\text{‰}$  per 100-m). However, research on sub-cloud evaporation in the cascades found d-excess lapse rate for the windward and leeward equal to  $0.23\text{‰}$  and  $1.6\text{‰}$  per 100-m, respectively (Bershaw, Hansen and Schauer, 2020) to encapsulate our observations and provide some confidence in our lapse rates.

Effects of snowpack fractionation on  $^{18}\text{O}$  and  $^2\text{H}$  is largely muted across the ER due to large seasonal variations in oxygen and hydrogen isotope compositions of net precipitation as well as competing fractionation processes of depletion and enrichment over the course of the snow season. Sublimation increases heavy isotope concentration at the top of the snowpack when vapor pressure deficits and solar radiation are high and ample snow exists (Earman *et al.*, 2006). Results indicate a weakly defined model response surface to evaporative fractionation likely due to deep snowpack and relatively low PET. Despite this, the calibrated  $\delta$ -value for  $^{18}\text{O}$  ( $1.96\text{‰}$ ) falls only slightly below the  $2.7$  to  $7.5\text{‰}$  range defined by Ala-aho et al. (2017) to imply that enrichment in snowmelt via sublimation is still a potentially important process. Kinetic fractionation is coupled to sublimation. However, the relatively low effect of sublimation on snowmelt non-equilibrium enrichment (d-excess median change  $<0.4\text{‰}$ ) across the watershed corroborates work by Schlaepfer et al. (2014) who found no significant change in d-excess over time in snowpack in the Rocky Mountains, implying the amount of sublimation was too low to create much effect, or the condensation of night-time vapor compensates for any day time enrichment (Stichler *et al.*, 2001; Beria *et al.*, 2018).

Melt at the snowpack surface percolates downward through the snowpack, re-freezes, and subsequently melts again. The downward process of melt/freeze enriches the solid phase in heavier isotopes to deplete the residual melt water and, in combination with evaporative fluxes drawing vapor upward, homogenizes the snowpack isotopically over time (Friedman *et al.*, 1991; Taylor *et al.*, 2001). Homogenization of the snowpack over time is observed in the depth-resolved data collected in 2020 (Figures S5-7). Melt fractionation conserves isotopic mass balance over the course of snow ablation. As such, initial meltwater is depleted in  $^{18}\text{O}$  and  $^2\text{H}$  and leaves behind an enriched snowpack reservoir in  $^{18}\text{O}$  and  $^2\text{H}$ . As melt continues both the snowpack and the melt water enrich in heavier isotopes (Taylor et al., 2001; Taylor et al., 2002; Ala-aho et al., 2017; Beria et al., 2018). We observe and model these phenomena in the ER

and show, similar to Feng *et al.* (2002), that deeper and more persistent snowpack has a longer period of higher efficiency associated with the exchange of isotopes between ice and liquid water to promote larger oscillations in depleted to enriched meltwater as a function of melt fractionation (refer to Figure 6g). Therefore, at sub-seasonal timescales, deeper snowpack can initially offset some of the evaporative enrichment impacts on the snowpack surface to mask the effects of both fractionation processes early in the snowmelt history, while late in the snowmelt cycle, snowmelt fractionation has the potential to compound enrichment related to sublimation. In contrast, we see the effect of high melt fractionation efficiency not drive bulk enrichment in melt water where deep, persistent snowpack resides (refer to Figure 6f, location B). This is because maximum fractionation is very low in comparison to the large amount of depleted winter snow water stored. The maximum melt fractionation factor ( $\epsilon$ ) in the ER is 0.16‰ and is slightly below the estimates presented by Ala-aho *et al.* (2017) for a watershed with deep snowpack ( $\epsilon < 1‰$ ). This discrepancy is compounded by use of temporally evolving efficiency of isotopic exchange ( $\epsilon$ ) defined as the ratio of snow accumulation to melt rate (Feng *et al.*, 2002). Consequently, the relative influence of snowmelt fractionation is at a maximum at snowmelt initiation but declines over the melt period. Therefore, while snow fractionation perturbations related to sublimation and melt may be important to exiting snowmelt at short time scales, and lower in the landscape (see section 4.2), the net effect ( $< 0.4‰$  for  $^{18}\text{O}$  and d-excess) is significantly smaller than the seasonal and spatial variability of the input signal from net precipitation, and our estimates suggest fractionation processes in the snowpack can be largely ignored under such conditions.

## 4.2 Role of Topography and Climate

Simulated water inputs of  $^{18}\text{O}$  and  $^2\text{H}$  into the ER are dominated by hydrological processes dictating the amount, timing, and phase of precipitation, which are dependent on landscape position and interannual climate conditions. The largest volumes of snowmelt occur in the upper subalpine, where deep and persistent snowpack produce a large pulse of the most depleted water in  $^{18}\text{O}$  and  $^2\text{H}$  entering the basin annually. At higher elevations in the alpine environment, more enriched summer rain falls in comparison to depleted, wind-scoured snowpack of lower accumulation. The LiDAR data allows us to implicitly account for wind-redistribution in the ER, but we do not estimate isotopic effects of wind. Given the possible enhancement of sublimation due to wind in the alpine environment (Comola *et al.*, 2017; Beria *et al.*, 2018), we are likely underestimating enrichment of snow in depositional areas. In fact, observed snowpit data at our highest elevation site during a wet water year was likely affected by wind in terms of its snow depth (4 m) and isotopically enriched surface layers extending to much greater depths than other, less wind affected sites (Figure S4). Nonetheless, the annual mass balance of water inputs resulted in higher  $^{18}\text{O}$  values compared to the conifer dominated regions in the subalpine. In the montane, seasonal isotopic inputs are controlled by delayed snowpack development and early snowmelt (Figure S10) and annually reflect estimated lapse rates

that enrich water inputs in  $^{18}\text{O}$  over all other inputs in the basin.

Hydrologic implications of canopy interception and evaporation were simulated. In the summer months, high atmospheric demand continually frees up canopy storage for more interception and the loss of relatively enriched rain in  $^{18}\text{O}$  back to the atmosphere biases the annual influx of net precipitation toward higher  $^{18}\text{O}$  values. The effect was greatest in the lower subalpine and montane and the consequence was to reduce the variability of annual isotopic inputs from precipitation across the watershed. In contrast, studies focused on intercepted snow by canopy in the intermountain western United States found higher  $^2\text{H}$  on the order of 13‰ and 2.1‰ for  $^{18}\text{O}$  with rates of enrichment increasing for smaller snow particles, denser canopy cover, longer residence times of storage and under clear-sky conditions (Claassen and Downey, 1995; Koeniger *et al.*, 2008). Despite possible implications of enriched throughfall on net water inputs, this was not modelled, and we may be underrepresenting evaporative fractionation in the forested regions of the ER and its effect on snowmelt. However, forest shading greatly reduces solar radiation on the snowpack surface (Musselman, Molotch and Brooks, 2008; Molotch *et al.*, 2009; Varhola *et al.*, 2010) and this influences snowmelt isotopic compositions through lack of evaporative fractionation adding ambiguity to any influence of enriched throughfall from canopy storage.

Declines in d-excess is a means to isolate sublimation effects from melt fractionation. Sublimation’s effect on bulk snowpack and associated snowmelt  $^{18}\text{O}$  and  $^2\text{H}$  values are largely controlled by the proportion of sublimation to snow accumulation. Subsequently, the effects of evaporation on snow isotopic signatures are largest in the upper montane where PET is high, shrub-dominated cover type is not sufficient to shade the snowpack from solar radiation, and snow accumulation is moderate and persistent enough such that sublimation losses are significant to the snowpack mass balance. In contrast, deep snowpack, vegetative shading, and low PET limit effects of sublimation on snowmelt isotopic inputs in the subalpine. Like the montane environment, alpine snowpack along southern aspects lacks shading, and a lower but persistent snowpack can result in a moderate effect of evaporative fractionation. However, low atmospheric demand limits sublimation losses and the effect of evaporative fractionation in the alpine environment remains relatively low. Observations at lower elevation indicate d-excess in snowmelt decreases 2x faster than at higher elevations (Figure 4). Simulated results suggest the rapid decline in d-excess at these lower elevations is related to phase shifts from snow to rain that co-mingle with melting snow to lower d-excess inputs as opposed to kinetic processes from sublimation.

Interannual climate variability influences  $^{18}\text{O}$  and  $^2\text{H}$  values of influxes primarily through altering the aridity gradient in the system and not through large changes in fractionation processes. This is exemplified through the lack of substantive change to d-excess between a wet and dry water year across all elevations, while changes in  $^{18}\text{O}$  appear largely controlled by small changes PET at elevation where the basin is energy-limited, and SWE. Specifically, under wet



conditions, SWE increases across the domain. The largest absolute increases in SWE occurs in the upper subalpine, but the largest relative increases in SWE occur in the high alpine and lower montane regions of the domain. Sublimation increases in a wet water year given additional snow accumulation and  $PET/P > 1$  but decreases where the basin is energy-limited. The result is a shift in the mass balance of the snowpack forcing more enrichment in heavy isotopes in the lower montane and less heavy isotopes at the highest elevations.

Results suggest limited effects of snowpack fractionation across the landscape and detailed observations of snowpack and snowmelt isotopic history in high elevation mountain systems may offer limited information. Instead, detailed observations of precipitation isotopic values are of greatest value, with emphasis on collecting these data at/above treeline where most of the snow resides. In addition, quantifying snowpack accumulation and timing of melt offers significant insight into the storage of depleted winter isotopes and the relative timing of these stores released into the terrestrial system.

### 4.3. Preferential Recharge Zone

Previous work in a sub-basin of the ER illustrated the importance of the upper subalpine as a zone of preferential recharge (Carroll *et al.*, 2019). In high alpine areas with low atmospheric demand, shallow soil storage and low permeable bedrock snowmelt was redistributed downgradient as shallow, ephemeral subsurface flow (interflow) into topographic convergent zones near the treeline. The subsidy of interflow into the upper subalpine was found to support the largest recharge rates and was partially decoupled from interannual climate variability to buffer the highest recharge rates during drought. Likewise, other studies have found the redistribution of snow, water and nutrients downslope toward tree-line amplified resource availability and buffered the eco-hydrologic system from interannual variability (Seastedt *et al.*, 2004; Knowles *et al.*, 2015). Our model does not contain the fully coupled groundwater model presented in our previous work since the focus for this research is on surface processes dictating water inputs into the soil zone to serve as an isotopic boundary condition flux for future work. However, hydrologic modelling does account for water partitioning in the soil zone between interflow, ET and recharge to estimate streamflow and help validate surface water influxes to the soil zone. Like previous work, we find the upper subalpine near treeline promotes the highest recharge rates in the basin, and that  $^{18}O$  values of influxes into the soil zone, averaged over multiple years, match groundwater  $^{18}O$  values observed across several sites. The influence of soil zone processes on isotopic signatures, as well as isotopic distinctions between mobile and immobile water and influences of mixing of water of different ages/tracer concentrations (Williams, 1989; Brooks *et al.*, 2010; Sprenger *et al.*, 2016; McDonnell, 2017; Zhou, Simunek and Braud, 2020) were not considered in defining groundwater recharge isotopic values. Excluding these processes likely introduces considerable uncertainty in our estimates (Sprenger *et al.*, 2019) and likely results in over-predicting d-excess in the groundwater. Future work will use stable water isotope boundary influxes to assess eco-hydrologic processes

more accurately, water routing and stream source across space and time within the ER.

## 5. CONCLUSIONS

This study represents a first attempt to model stable water isotope influxes into a large mountainous watershed at the temporal and spatial scales pertinent to quantifying energy and water balance of snowpack in complex terrain spanning nearly 2 km in topographic relief. The coupled hydrologic and isotope fractionation model is constrained with hydrologic observational networks as well as  $^{18}\text{O}$  and  $^2\text{H}$  data collected in precipitation, snowpack and snowmelt spanning multiple years and diverse climate conditions. Stable water isotope of influxes into the terrestrial system are dominated by the seasonal variability in precipitation amount, phase and isotopic value and associated elevational lapse rates. Fractionation processes are largely muted by deep snowpack, vegetative shading and low atmospheric demand that limit the effects of evaporative fractionation in the upper subalpine where most of the snow resides. Melt fractionation can have sub-seasonal effects on snowmelt with initial snowmelt depleted to potentially counterbalance any enrichment due to sublimation, but later snowmelt becomes relatively enriched in  $^{18}\text{O}$  and  $^2\text{H}$  through the isotopic mass balance of the remaining snowpack. Isotopic swings are relatively low compared to seasonal inputs from precipitation and are controlled by the efficiency of oxygen and hydrogen isotope exchange between ice and liquid water defined as a function of snow accumulation and melt rate which serves to reduce the effects of snowmelt fractionation as melt progresses. Simulated volume-weighted  $^{18}\text{O}$  inputs over a 5-year period in the upper subalpine agrees with groundwater observations to suggest this is a region of preferential recharge. The information is not definitive given the limitations in the modelling approach. However, in combination with previous studies, it provides additional evidence that deserves more exploration. Lastly, we suggest detailed, event-based precipitation monitoring of isotopes along an elevation gradient will provide the most important information needed to constrain isotopic mass flux into mountainous watersheds. Seasonal loading into the watershed greatly benefits from quantifying snow accumulation and ablation to define the delay and release of depleted winter isotopes across the landscape.

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Data Infrastructure for Virtual Ecosystem (ESS-DIVE DOI being generated).  
Supporting information provided as a separate document.

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Table 1. Isotopic model parameter values and method of assignment. MC = Monte Carlo.

Symbol	Equation	mean	rRMSE	Description	Units	Objective
O	1b	-0.16	-	$^{18}\text{O}$ precipitation lapse rate	‰ per 100 m	Observed (Fi
D	1c	0.96	-	d-excess precipitation lapse rate	‰ per 100 m	Observed (Fi
	2a, 2b	1.98	0.25	evaporative fractionation	‰	$^{18}\text{O}$ (melt &
	2a	-0.07	0.23	kinetic fractionation	dimensionless	$^2\text{H}$ & d-exces
	3a, 3b	0.15	0.34	snowmelt fractionation	‰	$^{18}\text{O}$ & $^2\text{H}$ (r
	3b, 4	0-1	-	snowmelt fractionation efficiency	dimensionless	see text, base

Figure 1: The East River (ER) study site with elevation and observation locations for isotopes, weather and stream discharge identified. Stream cells for the hydrologic model provided. Inset: The Colorado River Basin and ER in context of the western United States. Red circles (A-C) denote locations for model results in Figure 7.

Figure 2: (a) Observed snow water equivalent (SWE) for the period of record at a local Snow telemetry site with water years used in this study highlighted (2015-2020). LiDAR derived SWE (b) 30 March 2018 and (c) 7 April 2019. Lidar observations were not collected along the southern portion of the East River.

Figure 3. Precipitation isotopic inputs at site LMWL ( $P_p^i$ ). (a) Observed  $^{18}\text{O}$  as a function of phase and proximal SNOTEL air temperature. The same done for  $^2\text{H}$  (not shown). (b) Resulting linear functions for d-excess =  $^{12}\text{H} - 8 * ^{18}\text{O}$  and compared to observed data. (c) a comparison of the temperature function to estimate  $P_{p,t}^i$  over simulation time ( $t$ ) and observed data. (d) Mean differences in precipitation between the LMWL site and other locations ( $P_x^i$ ) as a function of elevation.

Figure 4. SWE-weighted snowpack observations (a)  $^{18}\text{O}$  and (b) d-excess; and 2017 snowmelt (c)  $^{18}\text{O}$  with snow pit values near peak SWE provided (loc 2892m based on 2016 data), and (d) d-excess. Slopes (m) provided as ‰ per day

Figure 5. (a) Resampled vegetation cover types at the 100 m grid resolution. Simulated annual fluxes for an average water year: (b) sublimation, mm (c)  $^{18}\text{O}$



of water influx to the soil, and (d) influence of snow fractionation processes on annual inputs of  $^{18}\text{O}$  defined as annual volume-weighted isotopic influx to the soil minus volume-weighted isotopic value of net precipitation.

Figure 6: Daily values at select sites for an average water year, 2016: (a) snow water equivalent, SWE (b) accumulated snowmelt, (c) melt fractionation efficiency,  $\epsilon$ , (d) precipitation  $^{18}\text{O}$  inputs, refer to equation 2b,  $P_{x,2}^i$ , (e)  $^{18}\text{O}$  water influx to the soil zone. (f) detail of  $^{18}\text{O}$  water influx from peak SWE to SWE=0 with slopes (m) provided, (g) change in  $^{18}\text{O}$  influx due to melt fractionation  $\Delta$ , (e) change in  $^{18}\text{O}$  inputs due to evaporative fraction  $\epsilon$ , and (f) change in d-excess (De) inputs due to kinetic fractionation  $\Delta$ . Positive values denote an increase and negative values denote a decrease in value. Locations provided in Figure 1.

Figure 7: Elevation averaged for a wet (2019) and dry (2018) water year: (a) differences ( ) between a wet and dry water year influx of  $^{18}\text{O}$  and d-excess normalized by removing net precipitation isotopic inputs, (b) average snow water equivalent, SWE, (c) potential evapotranspiration, PET, (d) aridity, or PET divided by precipitation (P), and (e) sublimation. Regression plots for  $^{18}\text{O}$  (f-i) and d-excess (j-m), for SWE, PET, PET/P and sublimation, respectively.

Figure 8. Elevation averaged (a) recharge, (b) annual volume-weighted  $^{18}\text{O}$  and (c) annual volume-weighted d-excess for water years 2016-2020. Range of observed groundwater isotopic observations and 2015 influxes indicated. Ecozones delineated with the upper subalpine preferential recharge zone 3600-4000 m identified.